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(54) Title: PROCESS FOR THE PRODUCTION OF A DETERGENT COMPOSITION (57) Abstract <p>A process for the production of a detergent powder composition having a bulk density of no more than 750 g/l, e.g. no more than 700 or 650 g/l, the process comprising mixing a particulate starting material which contains no more than 10 % by weight of the starting material of detergent active material and which starting material has a d₅₀ average particle diameter of from 100 µm to 1000 µm and a particle porosity of at least 0.4, together with a liquid component comprising a detergent active material or a precursor therefor in a mixer/granulator having both a stirring and a cutting action.</p>		

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PROCESS FOR THE PRODUCTION OF A DETERGENT COMPOSITIONTechnical field

5 The present invention relates to a process for the production of a detergent composition. In particular the invention is concerned with a process for the production of a detergent composition having a medium or low bulk density and to detergent compositions thereby produced.

Background to the invention

10 Conventionally, detergent compositions have been produced by a spray-drying process in which the components of the composition are mixed with water to form an aqueous crutcher slurry which is then sprayed into a spray-drying tower and contacted with hot air to remove water whereby detergent particles, often referred to as a "base" powder are obtained. The particles so obtained, have a high porosity. Thus powders produced by this method typically have a bulk density of 300 to 550 g/l or even up to 650 g/l.

Spray-dried powders generally provide good powder delivery characteristics such as dispensing and dissolution.

25 However, the capital and operating costs of the spray-drying process are high. Nevertheless there remains a significant consumer demand for such low density powders.

30 In recent years, detergent powders having a high bulk density have been produced by mechanical mixing processes. Bulk densities of 700 to 900 g/l and even higher have been obtained. Typically such powders are produced by densifying a spray-dried base powder in one or more mechanical mixers, optionally with the addition of further components, or by

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mixing the components of the composition in a continuous or batch mixing process without the use of a spray-drying step.

Powders having a high bulk density have a low packing volume which is advantageous for storage and distribution operations and also for the consumer. Furthermore, if a spray-drying step is not employed, the capital and operating costs are typically much lower and the process uses less energy and so provides an environmental benefit. The avoidance of a spray-drying step in the detergent production process is therefore often desirable.

However, such high density powders typically have a much lower porosity than a conventional spray-dried powder which may impair the delivery of the powder into the wash liquor. Additionally, the production of powders having a low to medium bulk density, for example less than about 700 g/l, has not hitherto been readily achievable on a commercial scale without the use of a spray-drying step.

EP-A-367 339 discloses a process for the production of a detergent composition having a high bulk density in which a particulate starting material is treated in a high speed mixer, a moderate speed mixer wherein the material is brought into or maintained in a deformable state, and then dried and/or cooled. The starting material may be a spray-dried base powder or the components of the composition may be employed without a prior spray-drying step in the detergent production process.

WO 97/02338 (Unilever : unpublished at the priority date of the present application) discloses that a low bulk density, for example less than 700 g/l, may be obtained by a process in which a spray-drying step is not employed, if the composition is formulated with a component having a low bulk

density. However, this process is relatively unsuitable for use with starting materials which are either available commercially in a form in which the particle density is high or which are themselves produced by spray-drying (the latter normally producing relatively porous particles).

We have now found that medium or low bulk density powders may be obtained by a new process of mechanical mixing of a powder which contains little or no detergent active material and which consists of particles having a predetermined average particle size and high particle porosity together with a liquid component comprising a detergent active material or a precursor therefor.

15 Definition of the invention

Thus, a first aspect of the present invention provides a process for the production of a detergent composition having a bulk density of no more than 750 g/l, e.g. no more than 700 or 650 g/l, the process comprising mixing a particulate starting material which contains no more than 10% by weight of the starting material of detergent active material and which starting material has a d₅₀ average particle diameter of from 100µm to 1000µm and a particle porosity of at least 0.4, together with a liquid component comprising a detergent active material or a precursor therefor in a mixer/granulator having both a stirring and a cutting action.

The present invention further extends to a detergent composition prepared by a process according to the present invention.

Detailed description of the invention

The present invention derives from the unexpected observation that the bulk density of the resultant product is dependent upon the rotational speed of mixing. This is also a function of the particular mixer of choice but essentially, the lower the speed of the mixer, the lower the bulk density of the product.

This new process has two distinct but separate advantages. The first advantage is that by choosing a powder starting material which already possesses the required average particle size and porosity medium or low bulk density powders may be prepared.

The second advantage is obtainable in manufacturing scenarios where both spray-drying and mechanical mixture agglomeration facilities are available. By affording the possibility of using a spray-dried product as a starting material in a mechanical agglomeration process, the present invention provides a further degree of flexibility in such a modular approach to the production of detergent powder products. As used herein, the abbreviation "NTR" means "non-tower route", i.e. a powder produced by mixing rather than in a spray-drying tower even if the starting materials are themselves produced by spray drying.

Suitably, the detergent composition resulting from the process of the present invention has a bulk density of 400 to 650 g/l, preferably 450 to 650 g/l and more preferably 500 to 600 g/l. It is further preferred that the resultant detergent composition has a particle porosity of at least 0.2 and more preferably at least 0.25.

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Suitably, the particulate starting material is dosed at a level of from 10 to 75 wt%, preferably from 20 to 40 wt%, of the composition resulting from the mechanical mixing process.

5

Instead of expressing particle size distributions in terms of average (e.g. d_{50}) particle diameters, if they are capable of being fitted to a Rosin-Rammler distribution, they may be expressed in terms of their Rosin-Rammler number. This is calculated by fitting the particle size distribution to an n-power distribution according to the following formula:-

10

$$R = 100 * \text{Exp} \left\{ - \left(\frac{D}{D_r} \right)^n \right\}$$

where R is the cumulative percentage of powder above a certain size D. D_r is the average granule size and n is a measure of the particle size distribution. D_r and n are the Rosin Rammler fits to a measured particle size distribution. A high n value means narrow particle size distribution and low values mean a broad particle size distribution.

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The process may be a continuous process or may be performed batch-wise.

One type of equipment suitable for carrying out the mechanical mixing comprises a high-speed mixer/densifier into which are dosed the starting material and the liquid component, to form a granular detergent material. In a preferred embodiment, the equipment further comprises a moderate-speed granulator/densifier into which the granular detergent material from the high-speed mixer/densifier is dosed and is thereby brought into or maintained in a deformable state and the resultant product is subsequently dried and/or cooled.

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An example of such a high-speed mixer/densifier is the Lödige (Trade Mark) CB 30 Recycler. This apparatus essentially consists of a large, static hollow cylinder having a diameter of about 30 cm which is horizontally placed. In the middle, it has a rotating shaft with several different types of blades mounted thereon. It can be rotated at speeds between 100 and 2500 rpm, dependent on the degree of densification and the particle size desired. The blades on the shaft provide a thorough mixing action of the solids and the liquids which may be admixed at this stage. The mean residence time is somewhat dependent on the rotational speed of the shaft, the position of the blades and the weir at the exit opening.

Other types of high-speed mixers/densifiers having a comparable effect on detergent powders can also be contemplated. For instance, a Shugi (Trade Mark) Granulator or a Drais (Trade Mark) K-TTP 80 may be used.

The components of the feedstock are thoroughly mixed in a high-speed mixer/densifier, preferably for a relatively short time of about 5-30 seconds.

After this first mix, the detergent material still possesses a considerable porosity, which can be desired for low density products. However, if further densification is required, instead of choosing a longer residence time in the high-speed mixer/densifier to obtain a further bulk density increase, it is preferred that detergent material is treated in a second processing step for about 1-10 minutes, preferably for 2-5 minutes, in a moderate-speed granulator/densifier. During this second processing step, the conditions are such that the powder is brought into, or maintained in, a deformable state. As a consequence, the particle porosity will be further reduced. The main

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differences from the first step reside in the lower mixing speed and the generally longer residence time of at least 30 seconds, for example 1-10 minutes, and the necessity for the powder to be deformable.

5

This second mixing stage can be successfully carried out in a Lödige (Trade Mark) KM 300 mixer, also referred to as Lödige Ploughshare. This apparatus essentially consists of a hollow static cylinder having a rotating shaft in the middle. On this shaft various plough-shaped blades are mounted. It can be rotated at a speed of 40-160 rpm. Optionally, one or more high-speed cutters can be used to prevent excessive agglomeration. Another suitable machine for this step is, for example the Drais (Trade Mark) K-T 160.

15

For use, handling and storage, the densified detergent powder must no longer be in a deformable state. Therefore, after the second mixing stage, the densified powder is dried and/or cooled. This step can be carried out in a known manner, for instance in a fluid bed apparatus (drying, cooling) or in an airlift (cooling). It is advantageous if the powder needs a cooling step only, because the required equipment is relatively simple and more economical.

25

When the two stage mixing process as described above is used, essential for the second and preferable for the first mixing stage is the attainment of a deformable state for the detergent powder in order to get optimal densification. The high-speed mixer/densifier and/or the moderate speed granulator/densifier are then able to effectively deform the particulate material in such a way that the particle porosity is reduced, and consequently the bulk density is increased.

35

Another suitable type of mixer/granulator for use in the process of the invention is bowl-shaped and preferably has a substantially vertical stirrer axis. Especially preferred are mixers of the Fukae (Trade Mark) FS0G series manufactured by Fukae Powtech Kogyo Co., Japan; this apparatus is essentially in the form of a bowl-shaped vessel accessible via a top part, provided near its base with a stirrer having a substantially vertical axis, and a cutter positioned on a side wall. The stirrer and cutter may be operated independently of one another, and at separately variable speeds.

Other similar mixers found to be suitable for use in the process of the invention are the Diosna (Trade Mark) V series ex Dierks & Söhne, Germany; and the Pharma Matrix (Trade Mark) ex T K Fielder Ltd., England. Other similar mixers suitable for use in the process of the invention include the Fuji (Trade Mark) VG-C series ex Fuji Sangyo Co., Japan; and the Roto (Trade Mark) ex Zanchetta & Co srl, Italy.

Granulation is preferably effected by running the mixer using both stirrer and cutter; a relatively short residence time (for example, 5-8 minutes for a 35kg batch) is generally sufficient. The final bulk density can be controlled by choice of residence time and stirrer rate.

Suitably the stirrer is operated at a rate of 25 to 250 rpm, e.g. from 100 rpm to 200 rpm or even as low as 30 to 50 rpm. However, this speed is dependent on the size of the apparatus. Independently the cutter is suitably operated at a rate of 200 to 3500 rpm, preferably 300 to 3000 rpm. For example, the cutter is suitably operated at a rate of 200 to 2500 rpm, preferably 300 to 2200 rpm. A batch process typically involves pre-mixing of solid components, addition

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of liquids, granulation, optional addition of a layering material suitable for controlling the granulation end-point, and product discharge. The rate of stirring and/or cutting is suitably adjusted according to the stage of the process.

- 5 The mixing step is preferably carried out at a controlled temperature somewhat above ambient, preferably above 30°C. Suitably the temperature is within the range 30 to 45°C.

- 10 The amount of detergent active material in the particulate starting material is no more than 10% by weight of that material. However, the amount of detergent active material in the particulate starting material is suitably no more than 5% by weight thereof and preferably no more than 1% by weight thereof. The particulate starting material may be
- 15 substantially or totally free of any detergent active material. Suitably, the particulate starting material may be one prepared by spray-drying. However, starting materials having the required parameters may be obtained by other means, e.g. involving granulation.

- 20 The d_{50} average particle diameter of the particulate starting material is from 100µm to 1000µm. This is important for controlling the particle size distribution in the final product. Preferably though, this average particle diameter
- 25 is from 150µm to 800µm, especially from 200µm to 700µm. Preferably, 90% by weight of the particles in the starting material have a particulate diameter in the region of 100µm to 1000µm.

- 30 The particle porosity of the particulate starting material is at least 0.4 but is preferably at least 0.45, e.g. from 0.45 to 0.55. Most preferably it is at least 0.50. In any event, such particulate starting material may comprise a spray-dried material, that is to say some or all of the
- 35 starting material is formed by a spray-drying process.

- 10 -

The measurement of particle porosity is based on the well known Kozeny-Carman relation for air flow through a packed bed of powder:

$$\frac{\phi_v h}{\Delta P} = k \frac{\pi D_{bed}^2}{4\eta} \frac{D_p^2 \epsilon_{bed}^3}{(1 - \epsilon_{bed})^2}$$

In which: ϕ_v = air flow
 ΔP = pressure drop over the bed
 D_{bed} = bed diameter
 h = bed height
 D_p = particle diameter
 ϵ_{bed} = bed porosity
 η = gas viscosity
 k = empirical constant, equal to 180 for granular solids

The bulk density of a powder can be described by the following equation:

$$\text{Bulk Density} = r_{sol} \cdot (1 - \epsilon_{bed}) \cdot (1 - \epsilon_{particle})$$

In which: r_{sol} = solids density of the materials in the particle
 $\epsilon_{particle}$ = particle porosity

Based on these equations, the particle porosity can be derived from the following experiments:

A glass tube with a diameter of 16.3 mm, containing a glass filter (pore diameter 40-90 μ m) as support for the powder, is filled with a known amount of powder (particle size between 355 and 710 μ m). The height of the powder bed is recorded. An air flow of 375 cm³/min is flowed through the bed of powder. The pressure drop over the bed is measured. The pressure drop over the empty tube should also be measured at the specified air flow.

This measurement is repeated with the same quantity of powder, but now a more dense bed packing is achieved by

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gentle tapping of the tube containing the powder. Again the pressure drop is measured at the specified air flow.

In order to be able to derive the particle porosity from these measurements, also the solids density of the particles is needed (eq. 2). This is measured using helium pycnometry, e.g. by using a penta pycnometer supplied by Quantachrome.

Based on the above described measurements and equations, the particle porosity can easily be derived.

10

For the purposes of the present invention, powder flow is defined in terms of the dynamic flow rate (DFR), in ml/s, measured by means of the following procedure. The apparatus used consists of a cylindrical glass tube having an internal diameter of 35 mm and a length of 600 mm. The tube is securely clamped in a position such that its longitudinal axis is vertical. Its lower end is terminated by means of a smooth cone of polyvinyl chloride having an internal angle of 15° and a lower outlet orifice of diameter 22.5 mm. A first beam sensor is positioned 150 mm above the outlet, and a second beam sensor is positioned 250 mm above the first sensor.

15

To determine the DFR of a powder sample, the outlet orifice is temporarily closed, for example, by covering with a piece of card, and powder is poured through a funnel into the top of the cylinder until the powder level is about 10 cm higher than the upper sensor; a spacer between the funnel and the tube ensures that filling is uniform. The outlet is then opened and the time t (seconds) taken for the powder level to fall from the upper sensor to the lower sensor is measured electronically. The measurement is normally repeated two or three times and an average value taken. If

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V is the volume (ml) of the tube between the upper and lower sensors, the DFR (ml/s) is given by the following equation:

$$\text{DFR} = \frac{V}{t} \text{ ml/s}$$

The averaging and calculation are carried out electronically and a direct read-out of the DFR value obtained.

- 10 The particulate starting material preferably comprises a builder, most preferably aluminosilicate, for example zeolite 4A or zeolite A24 or a salt, preferably an inorganic salt. Salts, preferably sodium, of phosphates, for example sodium tripolyphosphate (STP), carbonate, bicarbonate and
15 sulphate are also suitable.

- Other solid materials (if required) may also be incorporated in the particulate starting material, although they may alternatively or additionally be dosed at any appropriate
20 stage(s) of the mechanical mixing.

- The liquid component preferably contains at least one liquid nonionic surfactant. It may also contain one or more acid precursors of anionic surfactants and/or fatty acids. The
25 acid precursor(s) can then be neutralised to form the corresponding anionic surfactant(s) and the fatty acid(s) saponified by dosing one or more suitable alkaline materials at an appropriate stage during the mechanical mixing process. Suitable alkaline materials include alkali metal
30 carbonates, e.g. Na_2CO_3 and hydroxides, e.g. NaOH . Such alkaline materials may be dosed in solid form or as aqueous solutions. It is also possible to partially neutralise/saponify such precursors or fatty acids in the liquid component prior to the mechanical mixing step.

35

The detergent composition suitably comprise anionic detergent active. This may be incorporated as a pre-neutralised material, desirably as a component of the particulate starting material, or may be neutralised in situ. In the latter case the acid precursor of the active is preferably neutralised using a solid neutralising agent, for example carbonate, which is desirably a component of the particulate starting material.

10 The detergent active material present in the composition may be selected for anionic, cationic, ampholytic, zwitterionic or nonionic detergent active materials or mixtures thereof. Examples of suitable synthetic anionic detergent compounds are sodium and potassium (C_8 - C_{22}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10} - C_{15}) benzene sulphonates (LAS); sodium or potassium alkyl sulphates (PAS); and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum.

20 Suitable nonionics which may be employed include, in particular the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amines or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_8 - C_{22}) phenol ethylene oxide condensates, generally having 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of, 25 aliphatic (C_8 - C_{12}) primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 50 EO.

30 The level of detergent active material present in the composition may be in the range from 1 to 50% by weight depending on the desired applications. Nonionic material 35

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may be present in particulate starting material at a level which is less than 10% by weight more preferably less than 5% by weight and/or employed as the liquid binder in the mixing process optionally with another liquid component, for example water.

Suitably the particulate starting material constitutes 30 to 70% of the detergent composition.

Optionally, a layering material may be employed during the mixing step to control granule formation and reduce or prevent over-agglomeration. Suitable materials include aluminosilicates, for example zeolite 4A. The layering material is suitably present at a level of 1 to 4 wt %.

The composition may be used as a complete composition in its own right or may be mixed with other components or mixtures and thus may form a major or minor part of a final product. The composition may be blended with for example a spray-dried base powder. Conventional additional components such as enzymes, bleach and perfume may also be admixed with the composition as desired to produce a fully formulated product.

The present invention will now be further illustrated by the following non-limiting Examples.

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EXAMPLES

All Examples used the following equipment: a Fukae FS30 for batch NTR and a Lodige Recycler CB30 + Ploughshare KM300 for continuous NTR experiments.

Unless stated otherwise herein, all amounts expressed as percentages are on a weight basis and based on the total weight of the detergent composition or component prior to the addition of any post-dosed ingredients.

Production of zeolite-NTR powders according to the invention

The following slurries were spray dried to produce powders of high porosity and low bulk density (BD):

	Slurry 1	Slurry 2
	(wt%)	(wt%)
Zeolite A24	40.0	43.8
LAS	0.0	1.3
Sokalan CP5	10.0	5.0
water	50.0	49.9

The resulting powders had the following properties:

Properties	Base Powder 1	Base Powder 2
BD, [g/l]	629	370
DFR, [ml/s]	115	88
d ₅₀ [μm]	210	279
RRd [μm]	242	299
RRn [-]	2.7	2.4
Moisture Content [%]	5-7	7
Particle Porosity	0.51	0.70

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RRd = Rosin Rammler diameter

RRn = Rosin Rammler number

Sokalan CP5 is a polyacrylate/polymaleate copolymer.

5

The spray-dried zeolite-based porous carriers were subsequently used as base powders in NTR processes as described in Examples 1-8.

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Examples 1 & 2

Both base powders were used in a batch NTR trial on a Fukae. Base powder 2 was also used in a continuous NTR trial.

5.

Formulation	Example 1 (wt%)	Example 2 (wt%)	Reference (wt%)
Base Powder 1	43.4		
Base Powder 2		46.4	
Zeolite A24			46.4
PAS adjunct	31.9	33.8	33.9
Nonionic 7EO	9.4	10.0	10.0
Nonionic 3EO	6.3	6.6	6.6
Fatty acid	2.5	2.6	2.6
NaOH	0.6	0.7	0.7
Zeolite A24 layering	5.6	0.0	0.0
Premix			
Agitator rpm	200		
Chopper rpm	3000		
Time [sec]	10		
Granulation			
Agitator rpm	100		
Chopper rpm	3000		
Time [min]	1-0.5	1	1
Layering [sec]	10		
Powder properties			
DFR [ml/s]	140	90	55
RRd [μ m]	492-574	366	1015
RRn	2.6	1.9	1.6

The PAS adjunct used in the trial had the following composition:

PAS	45 wt%
Zeolite	38 wt%
Carbonate	9 wt%
Water + other components	8 wt%

10

Example 3

Base Powder 2 was also applied in a continuous NTR process, as a substitute for Zeolite A24. The following materials
5 were fed into the Recycler CB30:

Base Powder 2	46.3%
PAS adjunct	33.6
Nonionic 7EO	10.0
Nonionic 3EO	6.6
Fatty acid	2.2
50% NaOH soln	1.2

There was no additional densification step in the Ploughshare KM300 and in some cases the product from the
10 Recycler CB30 was fed directly into a fluid bed to cool. Depending on the recycler speed the following BDs and DFRs from the Recycler CB30 were obtained:

Recycler speed [rpm]	1500	1200	1000	800	500
BD [g/l]	620	570	544	502	436

15 This shows that the recycler speed can be used as a useful tool to control the final BD of the product.

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Examples 4-8

Porous zeolite base powder was granulated in a continuous NTR process.

5

Example	4	5	6	7	8	Control
Formulation (kg/h)						
Base Powder 2	459	458	458	458	457	
Control Carrier (zeolite A24)						422
PAS adjunct	330	332	331	331	330	331
Nonionic/fatty acid mixture	184	185	184	183	184	184
50% NaOH soln	12	12	12	12	12	8.5
Process parameters						
RPM (CB30)	1800	1500	1200	1000	300	1500
RPM (KM300)	120	120	120	120	120	120
Results ex Recycler CB30						
BD [g/l]	652	792	648	612	528	806
DFR [ml/s]	89	61	115	114	106	111
Results ex Ploughshare KM300						
BD [g/l]	748	689	687	670	457	908
DFR [ml/s]	77	81	85	90	130	124

A striking effect is caused by the speed of the Recycler CB30. The speed can be used to adjust the BD of the powder to the desired value, whereas at the same time still good particle size distributions are produced. With a standard zeolite having an average particle of from 0.5 to 30 μ m, it would not be possible to produce powders with very low Recycler CB30 speeds, as one will not get the right particle size distribution.

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Production of STP-NTR powders according to the invention

The following slurries were spray dried to produce powders of high porosity and low-BD:

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Composition	Wt%
STP (Rhodiaphos H5)	38.8
LAS	1.1
50% NaOH soln	0.3
45% Alkaline silicate soln	12.0
Water	47.9

The resulting powder had the following properties:

Properties

BD [g/l]	404
DFR [ml/s]	111
d ₅₀ [μm]	303
RRd [μm]	349
RRn [-]	2.9
Moisture content [%]	5.9
Particle porosity	0.67

- 10 The spray-dried STP-based carrier was used to formulate powders in Examples 9-13.

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Examples 9 & 10

The STP-based carrier was used in a batch NTR process using a Fukae FS30 mixer as follows:

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	Example 9 (kg)	Example 10 (kg)	Reference
Standard STP	0	0	4.7
Spray-dried STP carrier	4.7	4.7	0
Sodium carbonate	5.2	5.2	5.2
Zeolite 4A (Wessalith P)	1.0	1.0	1.0
LAS acid	3.3	3.3	3.3
Zeolite 4A layering	0	0.3	0
Pre-mixing			
Pre-mix time (sec.)	10	10	10
RPM (agitator/chopper)	100/3000	100/3000	100/3000
Mixing			
RPM (agitator)	100	200	100
RPM (chopper)	3000	3000	3000
Mixing time (sec)	120	120	120
Powder properties			
BD [g/l]	576	688	846
DFR [ml/s]	110	119	132
RRd [µm]	486	373	680
RRn [-]	1.72	1.70	1.19

Again the powders produced with porous carriers have a lower BD and a narrower particle size distribution as indicated by the higher RRn value.

Examples 11-13: Continuous NTR granulation with porous STP carrier

5 The STP-based carrier was used in a continuous NTR process using a Recycler CB30/Ploughshare KM300 as follows:

	Formulation (kg/h)		
	Example 11 (kg)	Example 12 (kg)	Example 13 (kg)
Spray-dried STP carrier	316	316	316
Sodium carbonate	340	340	340
Zeolite 4A	101	99	99
LAS acid/water	249	249	249
	Recycler CB30		
RMP	1500	1000	1800
	Ploughshare KM300		
Zeolite 4A layering [kg/h]	30	50	50
RPM	120	120	120
	Powder properties		
10 BD after Ploughshare [g/l]	481	522	649

CLAIMS:

1. A process for the production of a detergent powder composition having a bulk density of no more than 750 g/l,
5 the process comprising mixing a particulate starting material which contains no more than 10% by weight of the starting material of detergent active material together with a liquid component comprising a detergent active material or a precursor therefor in a mixer/granulator having both a
10 stirring and a cutting action characterised in that the starting material has a d_{50} average particle diameter of from 100 μ m to 1000 μ m and a particle porosity of at least 0.4.
2. A process according to claim 1 characterised in that
15 the bulk density of the product detergent powder composition is controlled to a predetermined value by setting the operational speed of the mixer/granulator.
3. A process according to claim 1 or claim 2 characterised
20 in that the starting material has a d_{50} average particle diameter of from 150 μ m to 800 μ m.
4. A process according to any preceding claim characterised in that the starting material has a d_{50} average
25 particle diameter of from 200 μ m to 700 μ m.
5. A process according to any preceding claim characterised in that the starting material comprises a material formed by spray drying.
30
6. A process according to any preceding claim characterised in that the mixer/granulator is a high speed mixer/densifier into which are dosed the starting material and the liquid component to form a granular material.
35

- 24 -

7. A process according to claim 6 characterised in that the material produced by mixing is subsequently dried and/or cooled.
- 5 8. A process according to any preceding claim characterised in that the mixer/granulator comprises a bowl-shaped vessel and a stirrer which rotates about a vertical stirrer axis or a horizontal hollow cylinder with in the middle a rotating shaft with blades.
- 10 9. A process according to any preceding claim characterised in that the particle porosity of the starting material is at least 0.45.
- 15 10. A process according to any preceding claim characterised in that the particle porosity of the starting material is at least 0.50.
- 20 11. A detergent powder composition prepared by a process according to claim 1.
12. A composition according to claim 11 characterised by a bulk density of no more than 700 g/l.
- 25 13. A composition according to claim 11 characterised by a bulk density of no more than 650 g/l.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/EP 97/06073

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C11D 17/06, C11D 11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CLAIMS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0367339 A2 (UNILEVER NV), 9 May 1990 (09.05.90) --	1-13
P,A	WO 9702338 A1 (UNILEVER PLC), 23 January 1997 (23.01.97) --	1-13
A	EP 0544365 A1 (UNILEVER N.V.), 2 June 1993 (02.06.93) -----	1-13

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Further documents are listed in the continuation of Box C.

☒

See patent family annex.

* Special categories of cited documents

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

Z document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/EP 97/06073

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0367339 A2	09/05/90	AU 616811 B AU 4393289 A CA 2001535 A,C DE 68925938 D,T ES 2085273 T IN 170497 A JP 2173099 A JP 7059719 B PH 26105 A US 5133924 A	07/11/91 10/05/90 02/05/90 08/08/96 01/06/96 04/04/92 04/07/90 28/06/95 06/02/92 28/07/92
WO 9702338 A1	23/01/97	AU 6416896 A GB 9513327 D	05/02/97 00/00/00
EP 0544365 A1	02/06/93	AU 647681 B AU 2854692 A AU 2854792 A BR 9204571 A BR 9204572 A CA 2083331 A CA 2083332 A CN 1073713 A DE 69203217 D,T EP 0544492 A ES 2075600 T HU 9203707 D JP 2060046 C JP 6017098 A JP 6100899 A JP 7039599 B KR 9513924 B KR 9601021 B MX 9206809 A NZ 245202 A SK 349592 A ZA 9209184 A ZA 9209185 A	24/03/94 17/06/93 27/05/93 01/06/93 01/06/93 27/05/93 27/05/93 30/06/93 30/11/95 02/06/93 01/10/95 00/00/00 10/06/96 25/01/94 12/04/94 01/05/95 18/11/95 17/01/96 01/07/93 22/12/94 10/08/94 26/05/94 26/05/94